ANALYSIS OF SAFETY AND PERFORMANCE STATUS OF DOUBLE-BASE PROPELLANTS BY HEAT FLOW CALORIMETRY

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ABSTRACT

Thermo-kinetic oscillations are among the most fascinating chemical oscillation reactions known in a system where significant temperature/pressure oscillations occur. The transport of heat out of the system is an essential part of the mechanism of the oscillation. The reaction causes the temperature/pressure to rise, and the rising temperature/pressure exerts a feed-back inhibition on the reaction to generate a feed-back loop (oscillation).

An oscillation phenomenon was observed during the microcalorimetric evaluation of 20 mm gun propellant. The heat flow began to gradually start a sinusoidal type oscillation after approximately 105 days of aging at 80ºC (~ 70% decomposition). The system resembles the Lotka model from 1910 with the variation that the autocatalytic reaction is substituted by a reaction with thermic acceleration, and the reaction which removes the autocatalytic substance is substituted by the transport of heat out of the system. The pattern of the oscillation is affected by internal gas pressure which is a function of the free head space of the test ampule. A possible similarity of the oscillation is suggested to the time-to-fume as determined by the NATO 65.5°C thermal stability tests used in other 20 mm propellants.

The scope of this paper is limited to a discussion of the relationship between the “time-to-oscillation” and the “time-to-fume” during the accelerated aging of 20 mm gun propellant.

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INTRODUCTION AND BACKGROUND

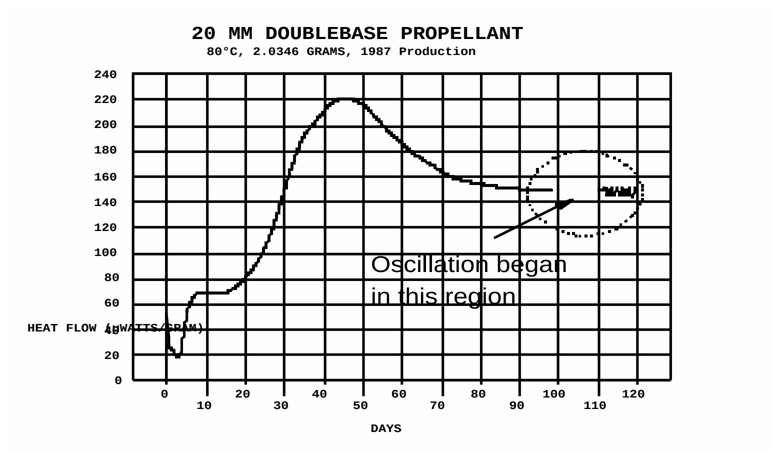
Gun propellant contains nitrate esters (nitrocellulose, nitroglycerin, or both). Nitrate esters are unstable. During the course of storage, it slowly and spontaneously releases nitrogen oxides (some are red color fume). Stabilizer is added to the propellant at the time of manufacturing to serve as a "trap" for the oxides. Without the stabilizer, or the stabilizer is nearly consumed, the liberated nitrogen oxides can catalyze the decomposition of the original nitrate esters. This reaction is exothermic and can eventually lead to autocatalysis (self-ignition) of the gun propellant. Propellants are subjected to test throughout their life time to assure that they remain in a stable condition safe for storage and handling.

Since 1988, NSWC Crane Division has been involving in developing a method using Microcalorimetry which can determine the safety storage life of various energetic compositions [1]. The method simplifies the interpretation of the data, and provide more realistic results for the prediction of thermal safety of the gun propellants. Microcalorimetry, when used with in conjunction with HPLC (high pressure liquid chromatography) to assess what chemically is occurring during aging, provides a very accurate time frame for the remaining safety storage life of the gun propellants.

During the microcalorimetric evaluation of 20 mm gun propellant an oscillation phenomenon was observed . At approximately 105 days of aging at 80°C the microcalorimetric heat flow curve began to gradually start oscillating. Figure 1 shows the first heat flow curve which detected the oscillation. It was not clearly evident until several days later that a reproducible oscillation was occurring. Figure 2 confirmed that was happening. The pattern of the oscillation is affected by internal free head space (free volume) of the test ampule. A possible relationship of the “time-to-oscillation” is suggested by comparing the “time-to-fume” determined in the NATO 65.5°C thermal stability test of similar 20 mm propellant.

CONDITIONS FOR OSCILLATION

Three conditions are required for the oscillatory behavior [2]. They are 1). The reactions must not be near thermodynamic equilibrium; 2). There must be a species that is autocatalytic; and 3). There should be two steady states for the system at its initial conditions. Although oscillations are most readily apparent in open system, closed systems also may show such behavior for a limited time, until thermodynamic equilibrium is achieved.



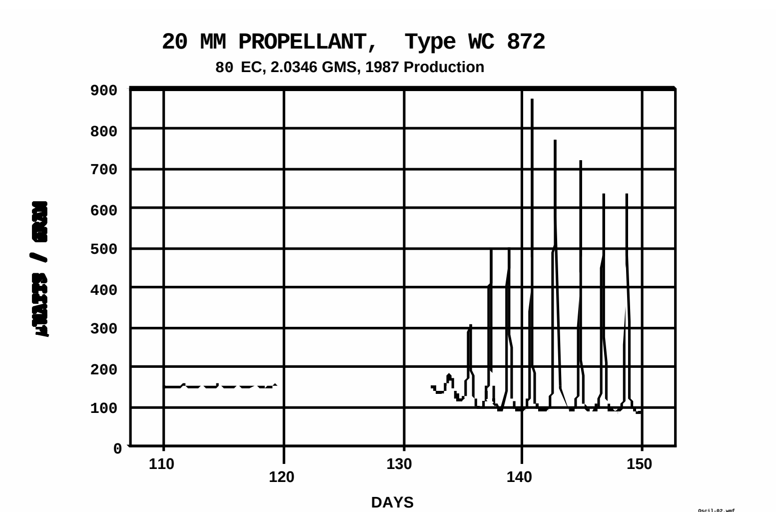


Figure 1 (Upper) First indication of oscillation occurring during evaluation of 20 mm double base propellant
Figure 2 (Lower) Confirmation of oscillation in heat flow curve of double base propellant

EXPERIMENTAL

1. Samples:

The test samples were from 20 mm Semi-Armor Piecing High Explosive Incendiary (SAPHEI) cartridges.. The cartridge contains about 38 grams of WC 872 formulation double base gun propellant. The selection was based on the year of production.

2. Instrumentation:

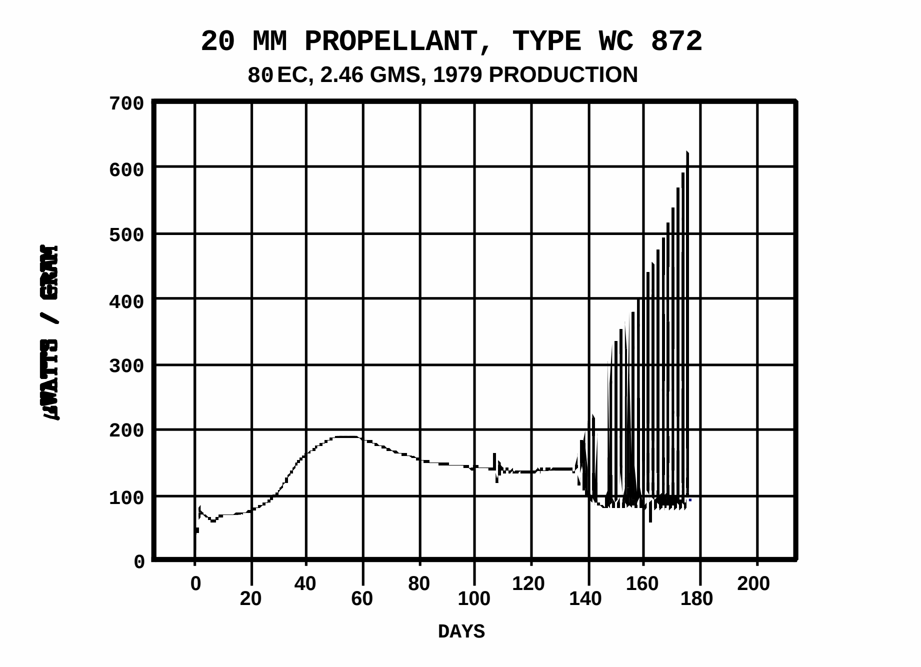
Microcalorimetric Analysis: The ThermoMetric Model 2277 Thermal Activity Monitor (TAM) microcalorimeter was used in this analysis. The TAM is equipped with 4 ampule calorimeters of differential type with a sample and a reference heat detector for effective suppression of thermal noise. The baseline stability over 8 hours at 25°C is within the Å 0.05 &W in static mode, and Å 0.5 &W in liquid flow mode. The sample container capacity is between 4 to 25 ml. The data represented herein was obtained using 4 ml stainless steel ampoules.

3. Experimental Approach:

Sample size was from 2.0 to 4.5 grams. The test ampule has a capacity of 4.5 grams of double base 20 mm ball propellant. The microcalorimetric analyzes were performed at 65.5, 75 and 80°C. Details of the experimental parameters have been reported [3]. The initial experimental testing was designed to optimize the results to obtain heat flow curves for obtaining kinetic information. It was not designed to determine the cause of the oscillations that were found. Sample size was maximized in later testing to control variations in heat flow if the test ampules are not filled to minimize head space.

RESULTS AND DISCUSSIONS

During the microcalorimetric evaluation of the propellant an oscillation in the heat flow curve was observed after 100 days aging at 80°C. The reproducibility of the oscillation was not understood until it was seen in other samples from different lots. Figures 3 through 4 illustrate the oscillation effect in other lots of propellants. Figure 5 is an expanded view of Figure 4. The heat flows are more erratic. This supports earlier work the heat flow is affected by sample size and internal head space [4]. Since the available head space will directly affect the magnitude of pressure built up in the closed ampule, the oscillations are more complex than those found when there is no significant head space. Figure 6 shows the inner ampule pressure as a function of time and the oscillation.



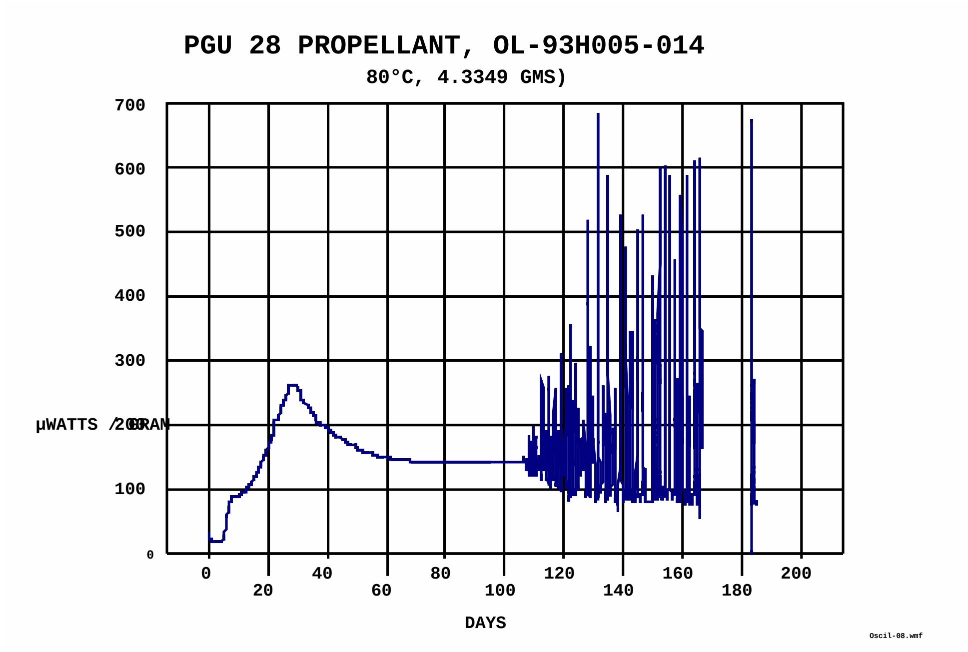
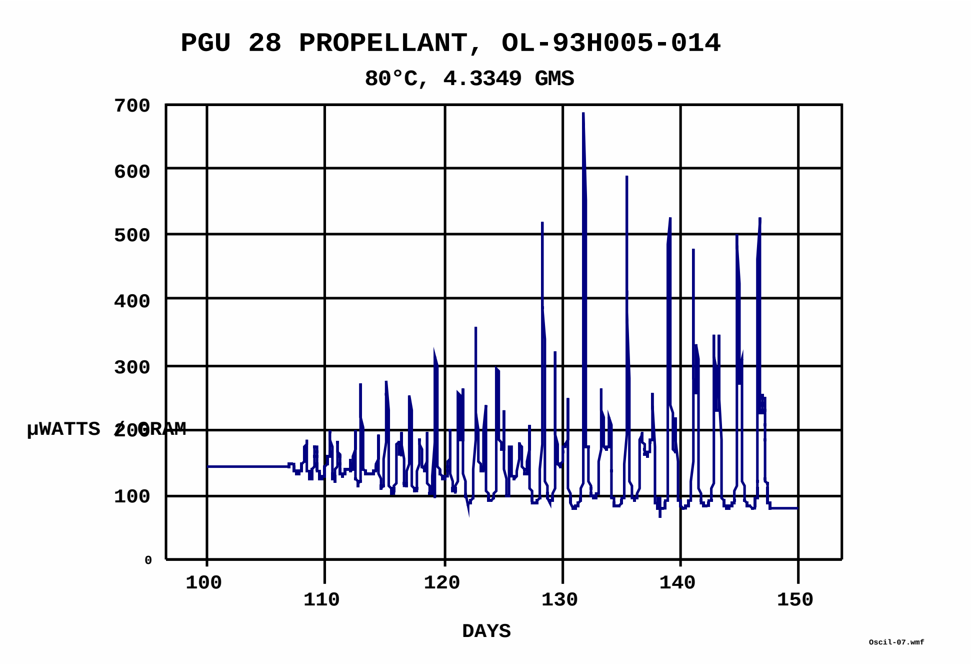


Figure 3 (Upper) Reproducibility of oscillation effect
Figure 4 (Lower) Oscillation observed in full test ampules



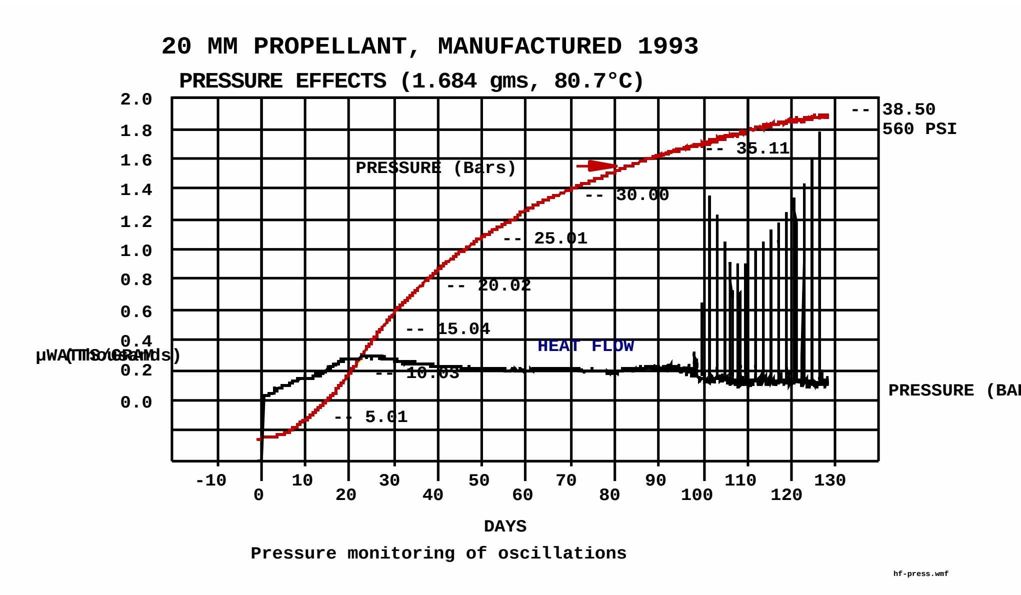


Figure 5 (Upper) Oscillation more erratic in shape when ampule is full
Figure 6 (Lower) Ampule pressure vs. Thermal Oscillation and Time

The first impression that occurs when considering the significance of these oscillations is comparing them with the days-to-fume from the NATO 65.5°C thermal stability test. Figure 7 is a combined plot of heat flow for 65.5 75, and 80°C. The maximum rate in these curve was chosen as the point of constant conversion. For the purposes of demonstrating the relationship of days-to-fume and the oscillation effect, the point of maximum rate for the nitrocellulose peak is used. The data in table 1 is plotted as the natural log of the time to peak maximum versus 1/T°Kelvin. If we know that the oscillation starts at 105 days then we can find the offset for that time and plot it on the same curve. The days-to-fume curve is offset by 1.2988 natural log units. The fume days are 202 for 75°C and 733 for 65.5°C. Figure 8 clearly illustrates this. Figure 9 is a plot of the frequency of fume days from Indian Head propellant database from WC 859 formulation which is similar to the WC 872 formulation of 20 mm propellant [5]. Both have the same nominal percent nitroglycerin content. Here we see that the expected days-to-fume are very close to that which was found by conducting long term tests. There are many factors which effluence the NATO 65.5°C test that result in wide spreads of the data. However microcalorimetric testing has shown a relationship between days-to-fume and this oscillation.

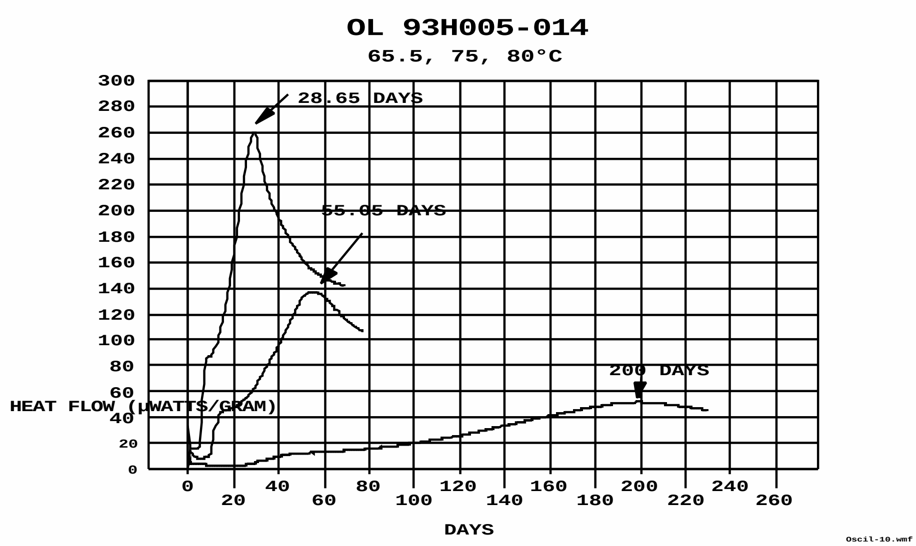


Figure 7. Kinetic data points from heat flow curves of 20MM double base propellants

Table 1. Calculation of Days-to-Fume from Kinetic Data of Microcalorimetric Heat Flow Curves

°C	1/T°Kelvin	NC Maximum Rate (Days)	Ln(Time to Peak)	Fume days Projected
65.5	.002952	200.00	5.3983	733
75	.002872	55.05	4.0082	202
80	.002831	28.65	3.3552	105
Ln offset to 105 days			1.2988	

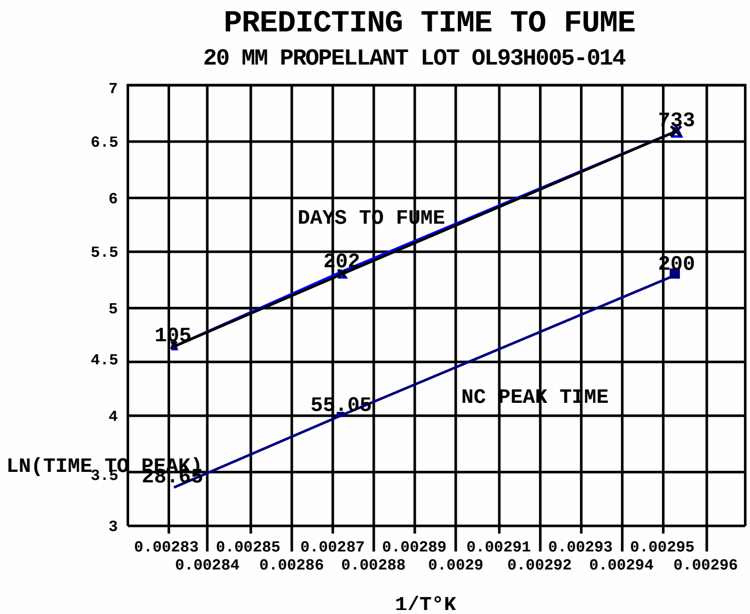
Kinetic Parameters

REGRESSION ANALYSIS

CONSTANT= -42.022
STANDARD ERROR OF Y EST.= 0.001055
R SQUARED= 0.99999
NO. OF OBSERVATIONS= 3
DEGREES OF FREEDOM= 1

X COEFFICIENTS(S) 16025.61 (SLOPE)
STANDARD ERR OF COEF. 12.09039

LN K=(-Ea/R)*(1/T°K)+LN A
R=1.98712 CAL/DEG/MOLE (GAS CONSTANT)
Ea= -R*(SLOPE OF ACTIVATION ENERGY PLOT)
Ea= 31,845 CALORIES/MOLE
PRE-EXPONENTIAL= 5.6 E-19



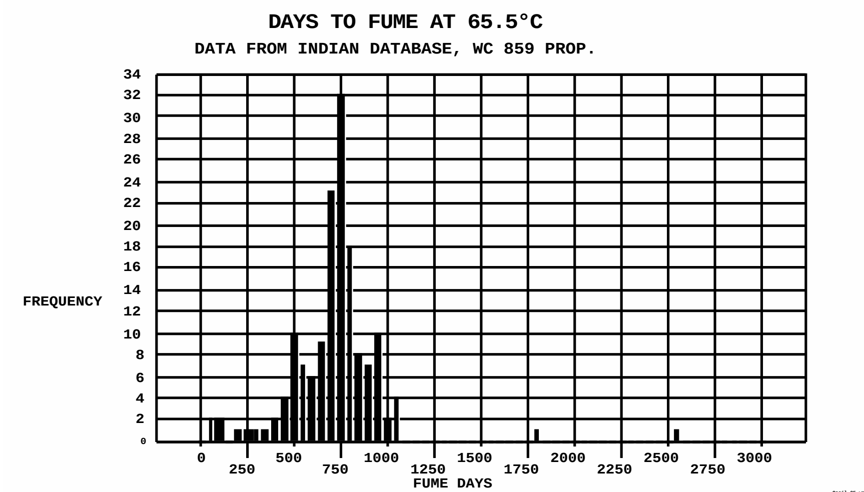


Figure 8 (Upper) Project Days-to-Fume from Microcalorimetric Heat flow data.
Figure 9 (Lower) Days-to-Fume from Indian Head propellant database for a similar 20 MM double base propellant

CONCLUSION

There is good correlation between the oscillations observed at 80°C and the reported days to fume at 65.5°C for similar 20 mm double base propellant. The microcalorimetry has much better control on experimental condition and superior data reproducibility (means less data spread). Most important of all, the microcalorimetry provide predictive capability for the safety and possible performance status for the propellants.

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